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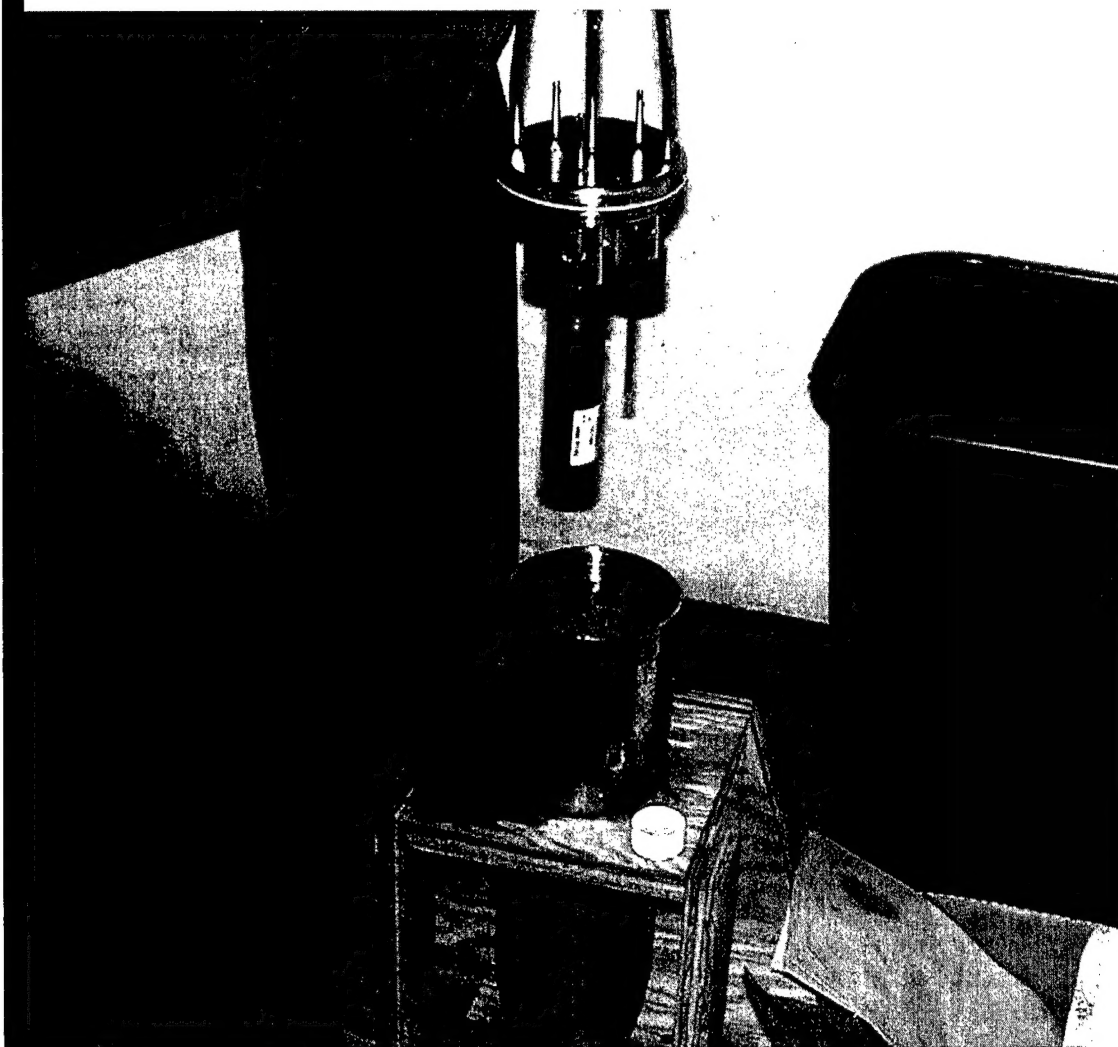
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Study of Five Discrete Interval-Type Groundwater Sampling Devices

Louise V. Parker and Charles H. Clark

August 2002



Abstract: Five relatively newly developed ground-water-sampling devices (the Kabis, HydraSleeve, Discrete Interval, Pneumo-Bailer, and USGS Passive Diffusion Bag [PDB] samplers) were tested to determine their ability to recover representative concentrations of a variety of analytes, including volatile organics, explosives, pesticides, and metals. The first phase of the study included several standpipe experiments with known concentrations of analytes. In the second phase, the devices were used in the field to sample TCE from a deep well and were compared with samples taken using low-flow sampling.

We found that the PDB sampler was the easiest device to use but should be used only for selected VOCs. The HydraSleeve and the Kabis Sampler are thief-type samplers that were also relatively easy to use. Although these devices could produce representative concentrations of explosives, pesticides, and metals in the standpipe experiments, they elevated the turbidity in our monitoring well. Therefore, we would recommend that their use be limited to wells where the turbidity is not affected by their use, especially if sampling for metals or the more hydrophobic organic

contaminants. In addition, there were small but statistically significant losses of some VOCs with the HydraSleeve in the standpipe studies (<5%) and of TCE in the field study (11%). Concentrations of VOCs taken with the Kabis Sampler did not show a substantial and consistent bias in either direction, except for the low-level study where loss of TCE was substantial, 18%. In the field study, loss of TCE was small (<8%) with this device and not statistically significant.

The Discrete Interval Sampler and Pneumo-Bailer are pressurized thief-type devices that are designed to collect a sample when activated. The Pneumo-Bailer was heavy and awkward to handle, required taking a nitrogen tank into the field, and was difficult to operate. The Discrete Interval Sampler required only a bicycle pump to pressurize the chamber, was smaller and lighter in weight, and easier to handle and operate than its counterpart. Both devices generally delivered representative concentrations of all the analytes tested in the standpipe experiments. Although loss of TCE was statistically significant for the Discrete Interval Sampler in the field study, loss was very small (<5%).

COVER: Kabis sampler

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PREFACE

This report was prepared by Louise V. Parker, Research Physical Scientist, Applied and Military Engineering Branch, U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire, and by Charles H. Clark, formerly a Research Technician in the Engineering Resources Branch, ERDC-CRREL.

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Study of Five Discrete Interval-Type Groundwater Sampling Devices

LOUISE V. PARKER AND CHARLES H. CLARK

1 INTRODUCTION

Ideally, a groundwater-sampling device should not alter the chemistry of the sample, be easy to use, and relatively inexpensive. However, a literature review on the effects of groundwater-sampling devices on sample integrity (Parker 1994 a, b) found that most devices, including the more commonly used bailers, peristaltic pumps and bladder pumps, can alter the chemistry of some samples for some analytes, especially analytes such as volatile organics (VOCs) and oxidizable inorganic constituents that are subject to precipitation reactions. There are a number of physical and chemical reasons why this is so. Change in temperature will affect the solubility and volatility of constituents and can cause degassing. A sample's temperature can change when it is brought to the surface, if either warm or cold air is entrained in the sample by the device, by heat generated by a pump, or from tubing exposed to hot or cold ambient air or intense solar radiation. Samples taken from deep wells undergo changes in pressure that can cause degassing of the sample. Air and other gases may be introduced into the well by the action of the device or inadvertently by agitation. Tubing and pump materials may sorb or leach analytes of concern. Once at the surface, volatiles and oxidizable contaminants may be lost as a result of aeration as the sample is dispensed into sample vials.

Theoretical and field studies over the last decade (Robbins 1989, Gibs and Imbrigiotta 1990, Martin-Hayden and Robbins 1991, Robbins and Martin-Hayden 1991, Gibs et al. 1993, Puls and Paul 1997), using multi-level samplers and other devices, have shown that with conventional sampling methods, concentrations in the well are typically integrated over the length of the screened interval and often reflect concentrations in the most permeable part of the screened interval. Therefore most methods that utilize large purge volumes or rapid pumping (for purging or sampling) do not produce information about the true concentration gradients within the aquifer. If the pumping rate or pumped

volume exceeds the rate of recharge by the aquifer, water can be pulled into the well from the most permeable zone, thereby giving misleading information on plume location and concentrations. In addition, studies of mobile colloidal particles revealed that high rates of pumping (for purging or sampling) or using devices such as bailers disturbed the aquifer and sand pack (Kearl et al. 1992; Puls and Powell 1992, 1997; Puls et al. 1992; Backhus et al. 1993). This disruption was caused by the stress of high water velocities or from surging due to sampling from bailers or high-speed pumps (Powell and Puls 1997). These stresses can cause grain flow within the sand pack and exceed the cohesive forces of aquifer mineral cementation resulting in artificially high turbidity (Powell and Puls 1997), which can increase the concentrations of metals and highly hydrophobic organic contaminants such as PCBs and pesticides (Puls and Powell 1992, Powell and Puls 1997, Backhus et al. 1993). Also, insertion of sampling devices can cause mixing between the screened and cased interval and adequate time is needed for equilibrium to be reestablished. To reduce these effects, dedicated pumps and low-flow (minimal drawdown) sampling is commonly used (Puls and Barcelona 1995, USEPA 1996), and more emphasis is being placed upon discrete interval sampling and shorter screened intervals within the well.

We recently surveyed the market to see what new products were available that allow discrete interval sampling and are less expensive to use than conventional slow-flow sampling protocols (using dedicated pumps) but which yield comparable results. We found several types of samplers that were designed for sampling discrete intervals within wells. Most were grab, or thief, samplers, including several pressurized systems that sample only when activated. The remainder were diffusion-based samplers that rely upon diffusion of analytes through a polymer membrane. All these samplers were designed to be used without purging or could be used without purging and thus assume that the flow in the well is horizontal and laminar. We selected five of these devices to study in more depth to determine whether they were able to recover representative samples as designed. It was not within the scope of this project to examine no-purge sampling per se. The five devices we selected were the Kabis Sampler (SIBAK Industries Limited, Inc.), HydraSleeve (GeoInsight), Solinst's Discrete Interval Sampler (Solinst Canada Ltd.), the Pneumo-Bailer (Best Environmental Subsurface Sampling Technologies, Inc. or BESST Inc.), and the USGS Passive Diffusion Bag (PDB) sampler (available through Columbia Analytical Services, Inc. or Eon Products).

Kabis Sampler

The Kabis Sampler is a bullet-shaped device made of type-321 stainless steel, and has a small collection tube and a longer, larger discharge tube at the top (Fig.

1). Depending upon the model or size of the sampler, it can hold either one or three VOA vials (Models 1 and 2) or a 1-liter sampler bottle (Model 3). Model 1 is 1.75 inches in diameter, approximately 20 inches in length, and weighs 6.2 pounds. Models 2 and 3 are 3.65 inches in diameter and 24 and 42 inches in length and 11 and 16.6 pounds in weight, respectively. The device is lowered into the well with a fiberglass tape. These devices reportedly can be used for sampling most types of analytes.

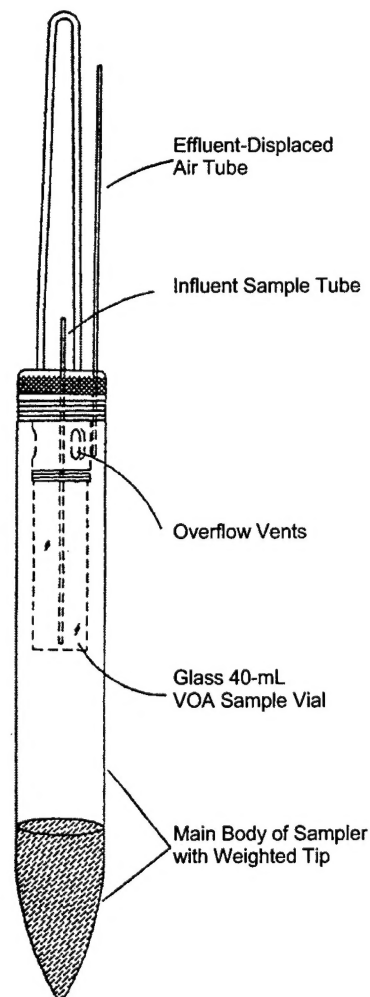


Figure 1. Kabis Water Sampler.

The manufacturer recommends that the sampler should be slowly and steadily lowered into the well. The inlet and exhaust ports are designed so that the sampler should not fill as it is being lowered into the well. Once the sampler has remained stationary for a few seconds, it begins to fill under hydrostatic pressure and the displaced air (or nitrogen if that was used to purge the system) escapes through the exhaust port. The sampling bottle rinses six times with formation water, which spills into the larger chamber underneath, prior to collecting the final sample. According to the manufacturer, the sample container is filled from the bottom up via laminar flow and in the absence of air, effervescence, splashing, and bubbling, thereby eliminating those sources of volatilization. The manufacturer also claims that turbidity is reduced by the hydrodynamic shape of the sampler and that the sample is collected under ambient pressure in the water column, which reduces or prevents loss of volatiles due to change in pressure or other analytes affected by atmospheric oxygen. Specially designed Teflon cone caps that eliminate the air space above the sample can be purchased for VOA vials. According to the manufacturer, other advantages are that the device is easy to operate, is readily decontaminated, and that purging is not required in most cases, thereby reducing the costs associated with using this device.

Disadvantages include that the preservative must be added after filling the sample container and that the device cannot be used in wells smaller than 2 inches. These devices are relatively expensive (when compared with disposable samplers), ranging from ~\$900 (Model 1) to \$2200 (Model 3).

Although we did not find any journal papers that examined the capabilities of this device, we did find an EPA report (Einfeld and Koglin 2000) that did so. They conducted a standpipe study in which they compared the ability of this device to recover six VOCs from test solutions. They tested this device in test solutions with both high (~200 µg/L) and low concentrations (10–20 µg/L) of the VOCs at two depths within the standpipe. Although they reported that there were no significant differences for 16 of the 24 comparisons they made, there were significant differences in eight instances. For five tests there was a negative bias, and for three tests there was a positive bias. Concentrations of 1,2-dichloroethane were higher than the controls in three tests (differences ranged from 11% to 18%). Concentrations of TCE and PCE were lower than the controls in four tests (all these losses were at the high concentration; mean losses were 19% and 32%, respectively). We observed that this loss appeared to correlate with Henry's constant for the VOCs tested, i.e., losses were greater for the more volatile compounds. They also reported that analysis of samples taken from a less contaminated layer that was below a more contaminated layer showed that this sampler appeared to either entrain contaminants from the dirty layer or collect a partial sample as it was lowered through the dirty layer. They also felt that this

device was moderately tricky to operate during the retrieval and preservation steps. In fact, we noted that the manufacturer recommends an hour of training.

HydraSleeve

The HydraSleeve is a cylindrical, flexible polyethylene bag with a polyethylene check ball at the top (Fig. 2). It is suspended from a line, is held together with stainless clamps, and has either a stainless steel or PVC weight attached to the bottom to keep it at the proper depth in the well. Currently, 350-mL-, 1-L- and 1.5-L-sized samplers are available, but other sizes can be readily manufactured. The 350-mL sampler is 1 foot in length and approximately 1.8 inches in diameter when full. The 1-L sampler is approximately 3 feet in length with the same outside diameter. This device reportedly allows discrete depth sampling of all types of analytes (VOCs, semi-volatile organics, metals, etc.) and is designed to be a no-purge system. The manufacturer's instructions recommend that the sampler be placed in the well and allowed to equilibrate for 24 hours prior to sampling. This equilibration time would allow for the well to return to its native state, air to vent from the sampler, and equilibration between the plastic bag and analytes in the well (i.e., sorption/desorption). The device is then raised and lowered approximately six inches twenty times to collect the sample. During the upstroke, the upper check valve opens and water moves into the flexible chamber, expanding it until it has filled. During the down cycle, the check ball seals. According to the manufacturer, once the bag is full, the internal pressure and floating ball keep the check valve closed as the device is recovered from the well.

The manufacturer claims that costs are reduced because the device is easy to operate; this reduces sampling time, especially if purging is eliminated. The device is relatively inexpensive, \$20–\$25 per sampler depending upon size, and this cost can be reduced by reusing the device in the same well.

To date, we have not found any published studies where the HydraSleeve has been evaluated.

Discrete Interval Sampler

The Discrete Interval Sampler and the Pneumo-Bailer both utilize positive pressure while the sampler is being lowered and raised to achieve discrete level sampling. According to the manufacturers, this prevents loss of VOCs during retrieval and prevents contamination from other layers during deployment and retrieval.

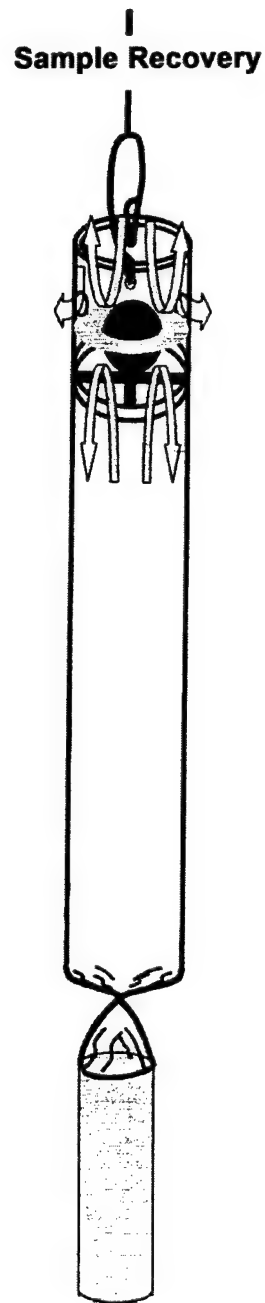
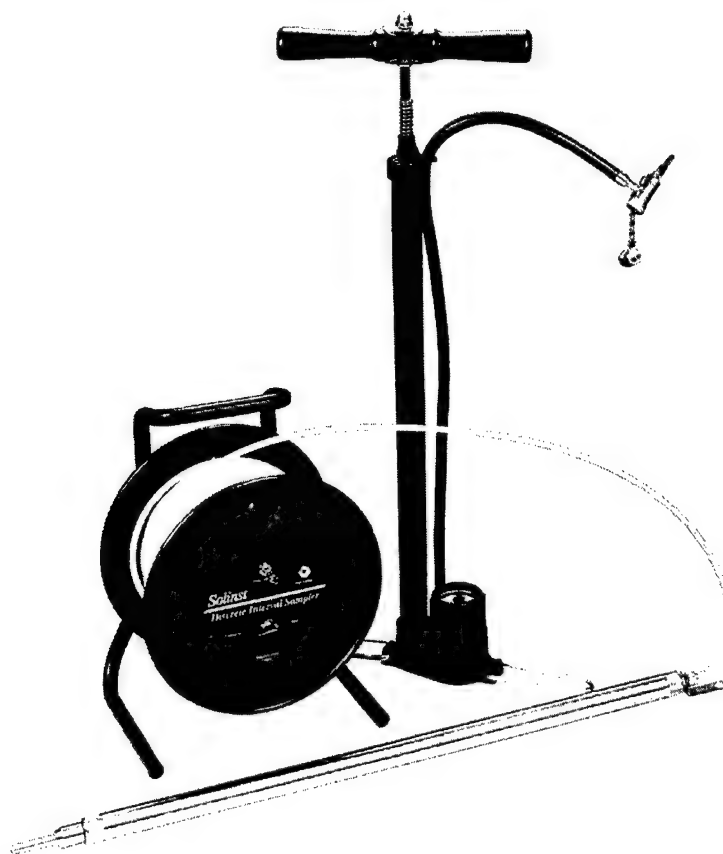


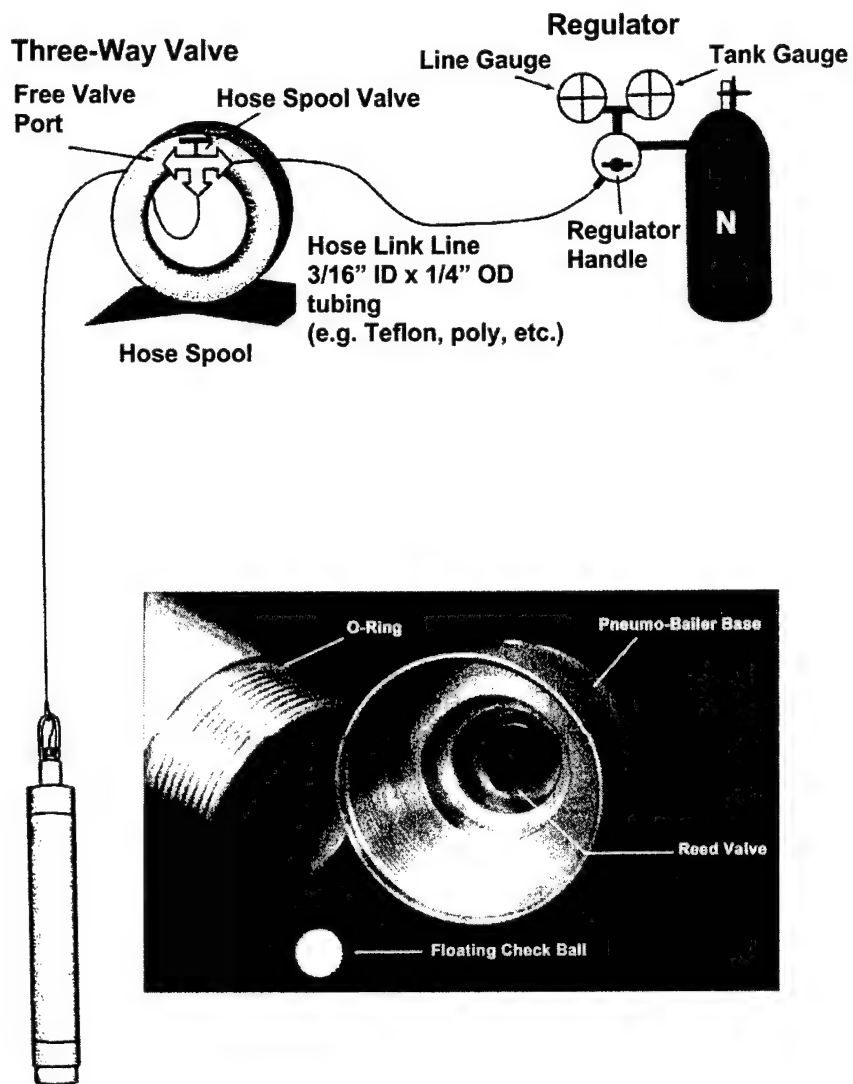
Figure 2. HydraSleeve.

Solinst's model number 425 (Fig. 3) is a stainless steel sampler with Viton O-rings. Airline tubing that runs from the surface to the sampler is typically LDPE (although Teflon and Teflon-lined polyethylene tubing are also available) and is mounted on a reel. The system is pressurized with a high-pressure hand pump that activates a pressure/vent switch. Once the desired depth is reached, the pressure is released and hydrostatic pressure allows the sampler and tubing to fill with water from the sample zone. The sampler is then repressurized and brought to the surface and the sample is decanted using a sample release device that, according to the manufacturer, is designed to prevent degassing of the sample. The price for this sampler is ~\$650. We have not found any published studies that evaluated this device.



a. Solinst model number 425.

Figure 3. Discrete Interval Sampler.



b. Stainless steel sampler with Viton O-rings.

Figure 3 (cont'd). Discrete Interval Sampler.

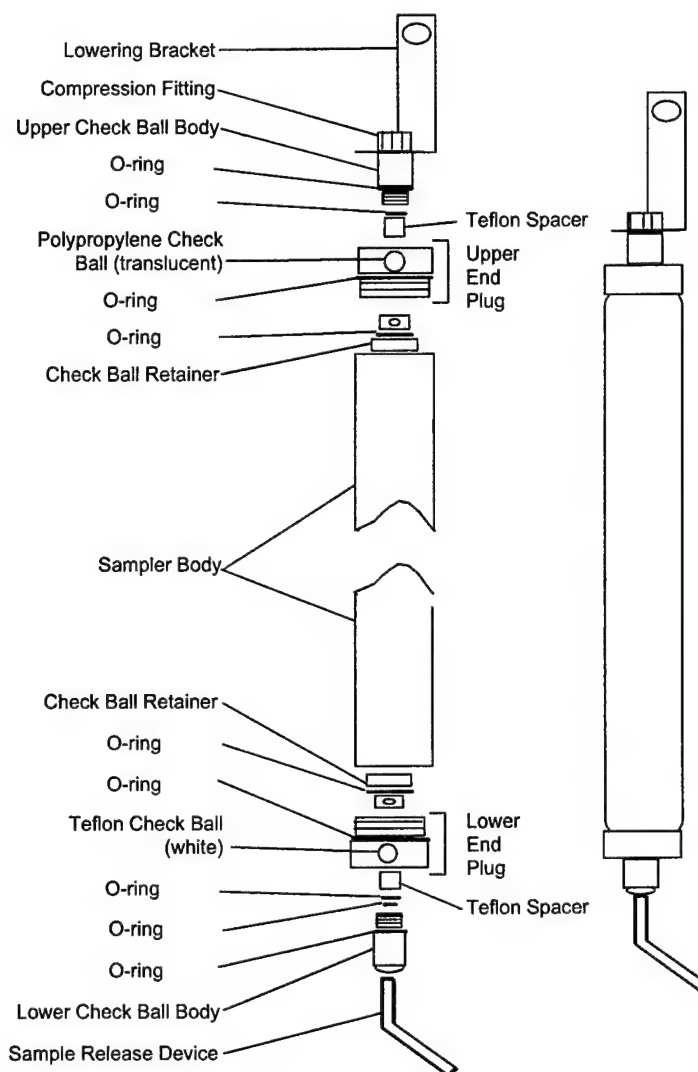


Figure 4. Pneumo-Bailer.

Pneumo-Bailer

The Pneumo-Bailer was designed specifically for recovering samples from deeper wells (100–1000 ft). The sampler has a stainless steel chamber with a Viton reed valve and two O-rings and a polyethylene floating check ball (Fig. 4). This device is connected to the surface with an LDPE gas-supply line and utilizes

nitrogen gas to pressurize the system during ascent and descent. Currently there are three models available: a 2-liter model and two 0.5-liter models with different outer diameters of 1.5 inch and 1 inch. Typically, this device is raised and lowered with an automated winch system. The price for these devices (plus spool for tubing and regulator) runs from \$1,050 to 1,800 (depending upon the model required). We have not found any published studies that evaluated this device.

Passive diffusion bag sampler

For the diffusion-based samplers, organic analytes permeate a plastic, or polymeric, membrane into a chamber that initially contained distilled or deionized water. Diffusion of analytes in and out of the device continues until equilibrium is reached. The time required to reach equilibrium depends upon the rate of exchange within the well, water temperature, the analyte, and the type of membrane. These samplers integrate analyte concentrations over time but are recommended for profiling discrete levels of contamination in the screened interval.

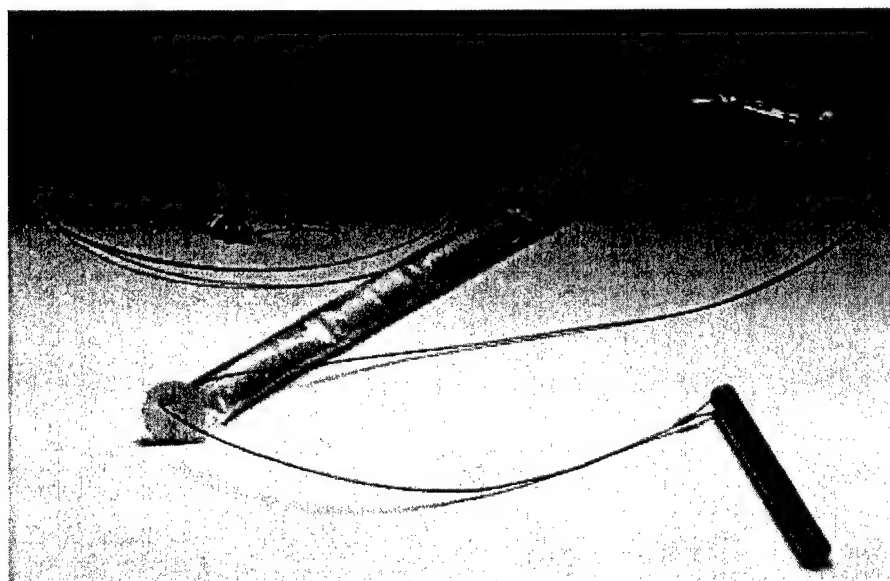


Figure 5. USGS passive diffusion bag sampler.

The USGS passive diffusion bag (PDB) sampler is among the more commonly known examples of this type of device. The PDB sampler (Fig. 5) is a cylindrical bag made of low-density polyethylene that is suspended on a weighted line (with a stainless steel weight). The PDB can also be purchased

with a polyethylene mesh covering to protect the bag from abrasion. Stainless steel or Teflon-coated stainless steel lines are recommended (Vroblesky 2001). These devices were developed by and have been well studied by Vroblesky and co-workers (Vroblesky and Hyde 1997, Vroblesky 2001, Vroblesky and Campbell 2001). According to USGS guidance (Vroblesky 2001), they are suitable for sampling most VOCs. However, they are not suitable for sampling inorganic ions and have limited applicability for non-volatile organic contaminants and even some VOCs (e.g., ketones, ethers, and alcohols) (Vroblesky 2001, Vroblesky and Campbell 2001). Vroblesky and Campbell (2001) found concentrations of ketones, ethers, and alcohols tended to be lower in the PDB samplers than in control samples.

Equilibration times for these devices in a well vary considerably with water temperature. For example, at 21°C, equilibration times (in closed vessels) for a number of VOCs (benzene, cis-1,2-dichloroethene, PCE, TCE, toluene) were 48 hours. However, at 10°C, equilibration times ranged from 52 hours for TCE and PCE to seven days for other compounds (vinyl chloride, 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,1-dichloroethane) (Vroblesky 2001, Vroblesky and Campbell 2001). The equilibration time of a closed system can be calculated using Fick's second law of diffusion, given by Crank (1975).

These devices are becoming popular because they are relatively easy to deploy, relatively inexpensive (\$22–\$30 per bag), and reportedly delineate stratification of contaminants well. Because they are disposable, they do not require decontamination and they reportedly eliminate or substantially reduce the amount of purge water required, thereby further reducing cost. These devices presumably would work well in formations with low permeability where it is difficult to obtain samples using other types of sampling devices. The pore size (~10 angstroms) of the polyethylene does not allow sediment to pass and this eliminates interferences from turbidity.

One of the disadvantages of using this type of device is that it takes several days to reach equilibrium, and therefore the sample reflects concentrations that have been in the well over that time period rather than the particular instance when the sample was taken. In addition, long-term deployment may result in biofilm development, which can slow transport across the film (Vroblesky 2001).

2 MATERIALS AND METHODS

General information

In the first phase of these experiments, the five devices were used to sample contaminated water in a standpipe. The water in the standpipe contained either mg/L or $\mu\text{g/L}$ concentrations of either several VOCs, explosives, pesticides, or metals. In the second phase of these studies, the devices were used to sample TCE-contaminated groundwater from one of our laboratory's deeper monitoring wells.

Standpipes

The standpipes used to hold the contaminated well water consisted of 8-inch-diameter, schedule-40 PVC pipe, approximately 8 feet long. For the bottom of the standpipe, a PVC end cap was pounded on one end; no organic solvent was used to join the end cap and casing.

Between experiments, the standpipes were cleaned using a high-temperature ($\sim 99^\circ\text{C}$) and pressure (1000 psi) washer with a 1% Liqui-Nox detergent solution, and rinsed with hot water until no more suds were observed. The standpipe was then filled and drained three times with deionized water.

Test solutions in the standpipe experiments

Explosives-contaminated water was obtained from Louisiana Army Ammunition Plant. Initial concentrations in the standpipe were approximately 2–5 mg/L for RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), 2,4,6-trinitrotoluene (TNT), and 1,3,5-trinitrobenzene (TNB), 500 $\mu\text{g/L}$ for HMX (octahydro-1,3,5,7-tetra-nitro-1,3,5,7-tetrazocine), and 100 $\mu\text{g/L}$ for 1,3-dinitrobenzene (DNB) and 2,4-dinitrotoluene (DNT).

The VOC and pesticide solutions were made by adding the neat chemical directly to deionized water in four five-gallon glass bottles. The solutions were stirred for up to three weeks using a magnetic stirrer. As expected, the pesticide solution took much longer to dissolve than the VOCs. Prior to pouring the pesticide solution into the standpipe, the solution was filtered through a glass-fiber filter to remove any undissolved particles of pesticide. The pesticide solution contained three analytes: lindane, aldrin, and dieldrin. These compounds were selected because they varied in their hydrophobic nature and propensity to adsorb

onto surfaces. Initial concentrations were approximately 500 µg/L for lindane, and 30–45 µg/L for aldrin and dieldrin.

Two VOC solutions were used in this study. In the low-level study, the test solution contained *trans*-1,2-dichloroethylene (TDCE), benzene (BENZ), trichloroethylene (TCE), *o*-dichlorobenzene (ODCB), *m*-xylene (M-XYL), and tetrachloroethylene (PCE). Initial concentrations ranged from 100 µg/L to 700 µg/L. In the high-level study, initial concentrations of BENZ, M-XYL, and PCE were approximately 130 mg/L.

For the metals study, the test solution was prepared by adding 3–7 mL of certified (GFS Chemical) metal standards (1,000 mg/L) directly to the standpipe. The solution was then mixed by recirculating it several times. Cd and Pb were in solution as cations, while Cr (as dichromate) and As (as arsenite or arsenate) were anions. Initial concentrations in the standpipe were approximately 70 µg/L for Pb, 50 µg/L for As and Cr, and 30 µg/L for Cd.

All the standpipes were filled with the test solution to within ~4–5 inches of the top. This allowed room to place the test device in the standpipe without spilling the test solution. During the initial equilibration period (prior to testing) and while the PDB samplers were left in the standpipe, the top of the standpipe was covered with a thin plastic disc that was held in place with duct tape and covered tightly with aluminum foil to reduce losses caused by volatilization from the standpipe.

TCE-contaminated monitoring well

The groundwater monitoring well used in this study had four-inch-diameter PVC casing and screen. The well is screened from 126.5 to 136.5 feet; the static water level was 125 feet. Concentrations of TCE in this well were around 130 mg/L. A dedicated Grundfos pump with Teflon-lined polyethylene tubing was used to retrieve the control samples from this well (pump intake was at a depth of 133 feet). Samples were taken using low-flow sampling (Puls and Barcelona 1995, USEPA 1996) at a flow rate of approximately 200 mL/min. No drawdown of the water level has been observed in this well at this rate of pumping.

Experimental design

For the standpipe experiments, the entry port for each sampling device was placed at the same depth as the sampling port on the standpipe. For the field study, the placement of the samplers in the well was matched in a similar fashion with the entry port of the groundwater pump. Each sampler went through the complete series of tests before the next type of sampler was tested. For the Kabis,

HydraSleeve, Discrete Interval Sampler, and Pneumo-Bailer, paired samples were taken by first taking a control sample, either from the standpipe or the well, and then one with the sampling device being tested. The number of paired samples varied with the type of analyte being studied and anticipated concentration. There were six paired samples in the VOC studies and in the field study, three in the explosives study, and five in the pesticides and metals studies.

In the field study, we gently removed the pump used to take the control samples prior to taking the next sample with the sampler being tested. In most cases, this was necessary because there wasn't enough room for both devices in the well. For the controls, turbidity readings were allowed to equilibrate prior to collecting a sample. Because of the time involved in allowing the well to re-equilibrate, no more than two types of devices were tested in one day. The first two sampling rounds with the HydraSleeve were taken on the first day. The remaining rounds with the HydraSleeve and all the rounds with the Discrete Interval Sampler were taken on day 2. All the rounds with the Pneumo-Bailer sampler and the first three rounds with the Kabis Sampler were taken on day 3. The remaining rounds with the Kabis Sampler were taken on day 5.

For the diffusion bag samplers, the protocol was different. For the standpipe experiments, three of the bag samplers were left in the standpipe for 1–3 weeks. Just prior to removing the bag samplers, three control samples were withdrawn from the sampling port. The bag samplers were then immediately taken to the laboratory (up two flights of stairs), the bags were punctured with a glass pipet, and the sample vials were filled using the pipet. In the field study, the control samples were obtained after the bag samplers were removed and the well was given time to equilibrate (~1 hour, with very low and stable turbidity readings).

Sample handling and analysis

Explosives

Samples were collected in 40-mL glass VOA vials with Teflon-lined screw caps. These vials were stored in a refrigerator overnight. The next day, an aliquot was transferred to a glass, 1.8-mL autosampler vial using a glass Pasteur pipet.

Analytical determinations were performed using reversed-phase HPLC (RP-HPLC) using a modular system as described by Parker and Ranney (1997a). Separations were obtained on a 150-mm × 3.9-mm (4-μm) LC-8 column (Waters) and eluted at 1.4 mL/minute with 85/15 (v/v) water/isopropanol (Walsh and Ranney 1999, Jenkins et al. 2001). The UV detector was set at 254 nm with the digital integrator operating in the peak height mode.

A combined explosives standard (8330 Calibration Mix #1) (Analytical Reference Materials Ultra Scientific) (1000 $\mu\text{g/mL}$ in acetonitrile) was diluted in HPLC-grade acetonitrile to yield 100 $\mu\text{g/mL}$. These standards were stored in the dark in a freezer. Working standards were made each sampling day by adding the diluted standard to deionized water to yield 2.5 and 0.25 mg/L .

Pesticides

Samples were collected in 43-mL glass vials with Teflon-lined plastic caps. Thirteen mL of sample were removed from each vial and discarded. The pesticides in the remaining 30 mL were extracted using pesticide-grade hexane according to a modified EPA Method #505 (US EPA 1991) as described by Parker and Ranney (1997b). After the hexane layer was carefully drawn off with a Pasteur pipet, any remaining water was removed by passing the hexane through a Pasteur pipet filled with glass wool and anhydrous sodium sulfate that had been washed with hexane. The dried hexane samples were then placed in 1.8-mL amber glass autosampler vials and stored at 4°C until they were analyzed.

Analyses were performed on a Hewlett-Packard (HP) 5890 series II gas chromatograph (GC) with an electron capture detector (ECD) equipped with an HP 6890 series autosampler-injector, all under the control of HP-Chemstation software. The GC was operated in splitless mode with 1- μL injections. The instrument was set with the following operating parameters: an injector temperature of 225°C, oven temperature of 200°C, detector temperature of 300°C, purge time 1 min. The column was a megabore multi-capillary SE-54 (Alltech), 1 m \times 2 μm film. The flow rate for the hydrogen carrier gas was 58 mL/min and 37 mL/min for the nitrogen makeup gas.

Each of the primary certified pesticide standards (Ultra Scientific) (1000 $\mu\text{g/mL}$ in hexane) was diluted with pesticide-grade hexane to yield 100 $\mu\text{g/mL}$. A combined standard of aldrin and dieldrin was made by adding 1 mL of each of the diluted standards into a 10-mL volumetric flask with hexane to yield 10 $\mu\text{g/mL}$. A combined standard containing all three pesticides was then made by adding 5 mL of the diluted dieldrin and aldrin standard and 5 mL of the more concentrated lindane standard to a 100-mL flask to yield 500 ng/mL dieldrin and aldrin and 5 $\mu\text{g/mL}$ lindane in hexane. Lower concentration standards were made by serially diluting the combined standard in hexane to yield 200 and 100 ng/mL of aldrin and dieldrin and 2 $\mu\text{g/mL}$ and 1 $\mu\text{g/mL}$ lindane. All the standards were kept in the dark in a freezer. The method detection limit (MDL) was obtained according to the EPA protocol as described in the Federal Register (1984).

Volatile organics

This section describes the methods used for the VOCs in the high-level and low-level VOC studies and for TCE in the field study. Samples were collected in glass 40-mL VOA vials, being careful to eliminate any bubbles or headspace, and sealed with Teflon-lined caps. These vials were stored in a refrigerator until the samples were analyzed. At that time, an aliquot was transferred to a glass, 1.8-mL autosampler vial using a glass Pasteur pipet. Most samples were analyzed within 24 hours and all within 48 hours.

Analytical determinations were performed using reversed-phase HPLC (RP-HPLC) using the same modular system that was employed in the explosives study. The UV detector was set at 215 nm, and separations were obtained on a 25-cm \times 0.46-cm (5- μ m) LC-18 column (Supelco) and eluted with 2.0-mL/min. of 65/35 (v/v) methanol/water. The detector response was obtained from the digital integrator operating in the peak height mode.

For the high- and low-level VOC studies, 2000 mg/L primary standards for each compound were made by adding a known amount of the neat chemical into methanol in a 50-mL glass volumetric flask and then weighing the flask. A mixed primary standard was made by adding 10 mL of the individual primary standards to methanol in 100-mL flasks (200 mg/L) in the low-level study or 20 mL of each individual primary standard (400 mg/L) in the high-level study. These standards were kept in the freezer. On analysis days, working standards were made by dilution of the mixed standard into deionized water. These standards ranged in concentration from 2.0 to 0.2 mg/L in the low-level study and from 20 to 150 mg/L in the high-level study. For the field study the standards for TCE were prepared in a similar fashion. Working standards in water ranged from 100 to 7.5 mg/L.

Metals

The items used in this study (e.g., high-density polyethylene [HDPE] sample bottles, polypropylene (PP) Eppendorf pipet tips and volumetric flasks, etc.) were acid-cleaned by soaking in a 10% solution (v/v) of nitric acid and deionized water for several days, rinsing with deionized water, soaking in deionized water for several more days, rinsing with deionized water, and air-drying. Samples were collected in HDPE sample bottles (10 mL) and were acidified with concentrated (redistilled) nitric acid to a pH of less than 1 (acid concentration 2% v/v). The chilled and acidified samples were sent in a cooler (with ice) by overnight delivery to another of the Engineer Research and Development Center's laboratories, the Environmental Laboratory in Vicksburg, Mississippi, for analyses. The

metals were analyzed by Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) according to SW 846 (US EPA 1994).

Statistical analyses

For each analyte in each study, paired t-tests (at 95% confidence level, $\alpha = 0.05$) were performed on the replicate samples taken with all the devices except the diffusion bag samplers. Because the tests with the diffusion bag samplers were more of a batch study, simple (randomized) t-tests were performed on those data sets. In all cases except for one, the data sets were found to be normally distributed (using a P value of 0.050), and thus did not require any transformation or the use of non-parametric statistical analyses. The one exception was the comparison between the arsenic concentrations in the PDB sampler (all below the detection limit) and the controls. That data set (using half the detection limit for the values in the PDB sampler) was not normally distributed, so a Mann–Whitney Rank Sum test was performed.

3 RESULTS AND DISCUSSION

Ease of use

The easiest sampler to use was the PDB sampler since all that is required is to place it in the well and then remove it after two, or more, weeks' equilibration. We used a glass Pasteur pipet to puncture the device and transfer the sample to a sample bottle. However, we found it difficult to control the flow into the bottle because the bag was flexible and tended to flop over. We found that it was easier to transfer the sample to a vial if the sampler was placed on a stand that held it upright. This allowed the individual taking the sample to have both hands free to collect the sample.

The HydraSleeve was lightweight and also relatively easy to operate. However, pouring the sample out of this device was also tricky for the same reasons and because the check valve had to be held open. We found it took two people to fill the sample vial; one person used a glass Pasteur pipet to hold the check valve open while the other held up the far end of the bag to help control the flow from the bag. Again, it might be better to transfer the sample to a vial by using a stand to hold the HydraSleeve upright and then puncture it as we did with the bag sampler. The manufacturer currently recommends obtaining a sample in this manner.

The Kabis Sampler was also easy to operate. The trickiest aspects of using this device were lowering it at a slow and steady rate and allowing enough time for it to fill. One advantage with this sampler was that once the sample was collected in the well, it did not have to be transferred to another container. However, because we tested one of the larger diameter devices, it was relatively heavy when it was full.

Operating the Discrete Interval Sampler was more complicated and took longer than the three previous samplers because it had to be pressurized prior to sampling and prior to retrieving the sample. However, it was much lighter in weight than its counterpart, the Pneumo-Bailer. We also found that this device was easier to bring into the field than the Pneumo-Bailer because all that was needed to pressurize this device was a hand pump, vs. bringing a gas cylinder into the field. We were able to control the flow of the sample into the sample bottle extremely well with both of these devices.

The manufacturer gives 28 steps for collecting a sample with the Pneumo-Bailer, and we found that this was the most difficult device to operate. There are several steps where you hook the tubing to the cylinder, then unhook it and re-

hook it and turn the gas cylinder on and off several times. We were constantly getting mixed up initially and even after having lots of practice, we had to be very careful not to get ahead of ourselves. In addition, this sampler was designed to take large samples and thus was heavy and awkward to handle. Although we didn't use a winch, we definitely recommend using one, especially for retrieving samples from deeper wells.

We were able to watch the devices while they were being used in the standpipe experiments. The PDB sampler caused only a slight disturbance when it was lowered into place but then was left to equilibrate for several weeks. The Hydra-Sleeve created bubbles as it went in and some during sampling but we found that raising and lowering it slowly reduced this. With the Kabis Sampler, we observed vigorous bubbling as it collected the sample. This appeared to disturb the water above the sampler, and the device banged against the walls of the standpipe. In contrast, the Discrete Interval Sampler and Pneumo-Bailer did not appear to disturb the water when they were lowered into the standpipe, and there was no bubbling of the water column above the sampler as the sample was collected.

Table 1. Initial turbidity readings following sampling.

Sample number	HydraSleeve*	Kabis Sampler*	Discrete Interval Sampler*	Pneumo-Bailer*
1	1.1	6.7	6.2	3.9
2	7.6**	18.8	4.0	1.0
3	7.1	7.8	3.3	4.4
4	9.5	7.8	2.6	2.1
5	7.6	28.0	2.5	4.0
6	4.8	25.6		1.1

* The samplers were tested in the following order starting with HydraSleeve, Discrete Interval Sampler, Pneumo-Bailer, and Kabis Sampler.

** One of the samplers was lost in the well and had to be retrieved. The turbidity remained elevated afterward.

In our field study, the HydraSleeve and Kabis Sampler elevated the turbidity levels more than the other samplers did (Tables 1 and 2). We believe that the up-and-down motion required to fill the HydraSleeve sampler was responsible for elevating the turbidity with this device. We also noted that the bottom edges of the HydraSleeve samplers were worn and one had a small leak in it. Because the Kabis Sampler was almost the same size as our monitoring well, it behaved like a piston pushing water in the well. We could hear and feel the water surging around the device as it entered the water and hear it hit against the wall of the

well as it collected the sample. We believe that the surging action and banging against the walls of the well were responsible for the elevated turbidity.

Table 2. Turbidity readings of the samples.

Sample number	HydraSleeve*	Kabis Sampler*	Discrete Interval Sampler*	Pneumo-Bailer*
1	1.0	3.6	7.6	2.6
2	8.8	3.0	3.6	2.4
3	8.2	5.2	2.6	1.0
4	7.4	6.3	1.4	1.8
5	6.7	3.3	1.6	0.6
6	9.9	1.7	2.1	2.2

* The samplers were tested in the following order starting with HydraSleeve, Discrete Interval Sampler, Pneumo-Bailer, and Kabis Sampler.

With respect to decontamination, the HydraSleeve and diffusion bag samplers are disposable and thus do not require decontamination. The remaining three devices were all relatively easy to decontaminate. Again, however, the size and weight of the Pneumo-Bailer made it more cumbersome to handle, and it required a larger cleaning vessel than the other devices.

Analytical results from the standpipe experiments

The complete data sets for the replicate samples for each sampler and study can be found in Appendix A, Tables A1–A6.

Explosives study

The variability between the replicate samples taken with the various devices was generally very low (Table 3). The late eluting 2,4-DNT had the highest relative standard deviations (RSDs), but even those were less than 8%.

There were no significant differences between the concentrations of explosives in the control samples vs. those collected with the Discrete Interval Sampler, HydraSleeve sampler, Kabis Sampler, or Pneumo-Bailer (Table 4). In contrast, even after 18 days' equilibration, representative concentrations of the explosives could not be obtained with the diffusion bag samplers. In fact, we did not detect any HMX or RDX in the bag samplers. It appears that the ability to recover these analytes corresponds roughly with the compound's molecular size, as the highest concentrations recovered were with the smaller DNB, then TNB,

and finally TNT. These results were not unexpected as USGS guidance (Vroblesky 2001) recommends that this device be used only for a specified list of VOCs.

Pesticide study

As expected with lower concentrations, the variability in this data set was greater than in the previous study. The RSDs ranged from 3% to 22% for the controls and all the devices except for the PDB samplers, where the RSDs ranged from 29% to 138% (Table 5).

There were no statistically significant differences between concentrations in the control samples vs. those taken with the HydraSleeve, Kabis Sampler, Discrete Interval Sampler, or Pneumo-Bailer (Table 4). Although there also was no significant difference between the control values and those found in the PDB samplers, mean concentrations in these samplers were substantially lower for two analytes (27% for aldrin and 66% for dieldrin) after 26 days' contact. Again, these findings support current guidance (Vroblesky 2001) that does not recommend using the PDB samplers for these types of analytes.

Volatile organics studies

The variability in these data sets was generally low with RSDs less than 5%, except for the late eluting PCE where RSDs ranged from 2 to 16% (Tables 6 and 7).

In both of these experiments, the Discrete Interval Sampler provided samples that were not significantly different from the controls (Table 4), although in the low-level study, loss of PCE was nearly 16% with this device.

In the low-level study, significantly lower concentrations of several analytes (TCE, ODCB, MXYL) were found with the HydraSleeve. However, in all cases these losses were minimal, less than 5%. There were no significant differences between the controls and sampler concentrations in the high-level study.

The results for the Kabis Sampler were mixed. In some cases, concentrations were significantly lower in the Kabis Sampler while in others the opposite was true. However, all these differences were small (<5%) except for loss of TCE (18%), which was one of the most volatile analytes in this study.

The results were also mixed for the Pneumo-Bailer. There were statistically significant differences for three analytes but these differences were very small, less than 2%.

Table 3. Summary for explosives study (concentrations in mg/L).													
		HMX		TNB		RDX		1,3 DNB		TNT		2,4DNT	
		Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler
Discrete Interval Sampler													
Mean	0.531	0.529	2.20	2.16	4.83	4.81	0.114	0.113	1.93	1.92	0.0958	0.0928	
S.D.	0.0068	0.013	0.02	0.01	0.057	0.092	0.001	0.002	0.017	0.024	0.0100	0.0005	
% RSD	1.3	2.4	0.8	0.5	1.2	1.9	1.0	1.9	0.9	1.3	7.3	0.5	
Pneumo-Bailer													
Mean	0.521	0.524	2.19	2.19	4.76	4.78	0.112	0.112	1.91	1.91	0.0925	0.0880	
S.D.	0.006	0.002	0.02	0.02	0.029	0.037	0.001	0.0002	0.01	0.007	0.0064	0	
% RSD	1.1	0.4	1.1	1.0	0.6	0.8	1.0	0.2	0.5	0.4	6.9	0	
HydraSleeve													
Mean	0.520	0.533	2.22	2.14	4.75	4.77	0.112	0.113	1.91	1.89	0.0922	0.0916	
S.D.	0.002	0.007	0.02	0.02	0.027	0.057	0.0002	0.0015	0.008	0.016	0.0030	0.0035	
% RSD	0.5	1.3	1.0	1.1	0.6	1.2	0.2	1.3	0.4	0.9	3.2	2.3	
Kabis Sampler													
Mean	0.522	0.521	2.25	2.24	4.77	4.76	0.112	0.113	1.92	1.92	0.0956	0.0992	
S.D.	0.008	0.011	0.02	0.03	0.040	0.092	0.0009	0.002	0.01	0.04	0.0055	0.0032	
% RSD	1.5	2.0	0.9	1.2	0.8	1.9	0.8	1.9	0.8	1.9	5.7	3.2	
Diffusion bag sampler													
Mean	0.532	All ND	1.88	0.356	4.8	All ND	0.112	0.097	1.87	0.873	0.375	0.089	
S.D.	0.002		0.005	0.004	0.14		0	0.0006	0.002	0.010	0.0006	0.002	
% RSD	0.3		0.3	1.3	3.0		0.0	0.6	0.1	1.1	0.2	2.3	
ND = non detects, below the detection level													

Table 4. Results of the statistical analyses comparing the various samplers and the percent difference from the control samples ¹ .												
Explosives standpipe study												
Sampler	HMX		TNB		RDX		1,3 DNB		TNT		DNT	
	Sign.	% Dif.	Sign.	% Dif.	Sign.	% Dif.	Sign.	% Dif.	Sign.	% Dif.	Sign.	% Dif.
Discrete Interval	NS		NS		NS		NS		NS		Not tested ²	
HydraSleeve	NS		NS		NS		NS		NS		Not tested ²	
Kabis	NS		NS		NS		NS		NS		NS	
Pneumo-Bailer	NS		NS		NS		NS		NS		Not tested ²	
Diffusion Bag	S	>-95% ³	S	-81%	S	>-99.5% ³	S	-14%	S	-53%	S	-76%
Pesticides standpipe study												
	Lindane		Aldrin		Dieldrin							
	Sign.	% Dif.	Sign.	% Dif.	Sign.	% Dif.						
Discrete Interval	NS		NS		NS							
HydraSleeve	NS		NS		NS							
Kabis	NS		NS		NS							
Pneumo-Bailer	NS		NS		NS							
Diffusion Bag	NS		NS	(-27%)	NS	(-66%)						

Table 4 (cont'd). Results of the statistical analyses comparing the various samplers and the percent difference from the control samples ¹ .												
Low-level (ppb) VOC standpipe study												
	TDCE		BENZ		TCE		ODCB		MXYL		PCE	
	Sign.	% Dif.	Sign.	% Dif.	Sign.	% Dif.	Sign.	% Dif.				
Discrete Interval	NS		NS		NS		NS		NS		NS	(-16%)
HydraSleeve	NS		NS		S	-2.9%	S	-4.9%	S	-4.9%	NS	NS
Kabis	NS		S	+1.5%	S	-18%	S	+1.2%	NS		NS	NS
Pneumo-Bailer	NS		NS		S	-1.4%	S	-1.8%	NS		NS	NS
Diffusion Bag	S	-9.7%	NS		NS		NS		S	+18%	NS	NS
High-level (ppm) VOC standpipe study												
	BENZ		MXYL		PCE							
	Sign.	% Dif.	Sign.	% Dif.	Sign.	% Dif.						
Discrete Interval	NS		NS		NS							
HydraSleeve	NS		NS		NS							
Kabis	NS		NS		S	-4.7%						
Pneumo-Bailer	S	-1.7%	NS		NS							
Diffusion Bag	S	+5.2%	S	+8.2%	S	+11%						
Metals standpipe study												
	Arsenic		Cadmium		Chromium		Lead					
	Sign.	% Dif.	Sign.	% Dif.	Sign.	% Dif.	Sign.	% Dif.				
Discrete Interval	NS		NS		NS		S	+5.9%				
HydraSleeve	NS		S	-4.2%	NS		NS					
Kabis	NS		NS		NS		NS					
Pneumo-Bailer	NS		NS		NS		NS					
Diffusion Bag	NS	(> -96% ⁴)	S	> -92% ³	S	-95%	S	> -98% ³				

Table 4 (cont'd).										
			Field Study							
			TCE							
	Sign.	% Dif.								
Discrete Interval	S	-5.4%								
HydraSleeve	S	-11%								
Kabis	NS									
Pneumo-Bailer	NS									
Diffusion Bag	S	-14%								
S = A statistically significant difference was found between concentrations in the control samples vs. samples taken with the test sampling device (at 95% confidence level).										
NS = No statistically significant difference was found between concentrations in the control samples vs. samples taken with the test sampling device (at 95% confidence level). However, the power of these tests was generally low and therefore negative findings should be interpreted with caution.										

¹ The mean percent difference from the control values is shown in bold print for samplers that were significantly different ($\alpha = 0.05$) from the controls. Percent differences were also given for samplers where no significant difference was found if the difference exceeded 15%. (We realize that these percent differences may not be reproducible since the difference between these two treatments was not statistically significant.) A negative number indicates concentrations were lower in the samples taken with the test device than in the control samples, whereas a positive number indicates concentrations were higher in the test device.

² There was insufficient data to perform statistical analyses.

³ Losses are based on the detection limit of the analyte.

⁴ The normality test for these data sets failed. There was no significant difference between these data sets by Mann-Whitney Rank Sum Test (95% confidence level, $P = 0.100$).

Table 5. Pesticide study summary.								
	Lindane			Aldrin			Dieldrin	
	Conc. (µg/L)			Conc. (µg/L)			Conc. (µg/L)	
Sampler	Control	Sampler		Control	Sampler		Control	Sampler
Discrete Interval Sampler								
Mean	594	541		30.3	29.6		47.2	45.6
Standard Deviation	106	92		5.9	5.1		2.4	3.4
% RSD	18	17		20	17		5.0	7.5
HydraSleeve								
Mean	510	563		29.9	30.2		45.5	47.7
Standard Deviation	113	82		3.3	4.6		4.4	4.7
% RSD	22	15		11	15		9.8	9.8
Kabis Sampler								
Mean	599	574		30.6	31.0		48.1	48.6
Standard Deviation	81	55		1.2	2.2		6.1	2.1
% RSD	14	10		4	7.2		13	4.4
Pneumo-Bailer								
Mean	573	513		32.2	32.2		45.8	43.1
Standard Deviation	77	60		5.0	4.8		3.7	1.4
% RSD	13	12		16	15		8.2	3.3
Diffusion bag sampler								
Mean	560	504		32.7	23.9		31.1	10.6
Standard Deviation	120	176		3.4	7.0		3.2	15
% RSD	21	35		10	29		10	140

Table 6. Summary of findings in the low-level VOC study (concentrations in µg/L).													
		TDCE		BENZ		TCE		ODCB		M-XYL		PCE	
		Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler
HydraSleeve													
Mean	339	334	521	513	647	628	729	693	177	169	88	85	
S.D.	6.3	8.4	7.8	7.5	12.8	9.6	6.5	6.1	6.3	5.0	1.4	7.3	
% RSD	1.9	2.5	1.5	1.5	2.0	1.5	0.9	0.9	3.6	2.9	16	8.6	
Kabis Sampler													
Mean	338	343	515	523	638	523	721	730	176	179	84	89	
S.D.	7.4	3.8	8.4	5.9	12	5.9	8.3	6.0	5.3	5.1	8.5	3.4	
% RSD	2.2	1.1	1.6	1.1	1.9	1.1	1.1	0.8	3.0	2.9	10	3.9	
Pneumo-Bailer													
Mean	363	357	549	544	690	680	776	764	189	188	95	92	
S.D.	11	9.4	5.8	8.2	8.3	12	8.1	16	5.0	6.6	13	8.2	
% RSD	3.1	2.6	1.1	1.5	1.2	1.8	1.0	2.0	2.7	3.5	14	8.9	
Discrete Interval Sampler													
Mean	359	360	562	563	694	698	802	807	194	196	101	85	
S.D.	7.4	5.0	8.9	4.6	15	6.8	10	3.8	6.7	6.1	3.0	18	
% RSD	2.1	1.4	1.6	0.8	2.1	1.0	1.3	0.5	3.4	3.1	3	21	
Diffusion bag sampler													
Mean	257	232	345	346	398	406	513	524	33	39	52	55	
S.D.	7.7	5.1	7.3	10	10	13	5.8	9.0	7.6	1.4	5.1	2.4	
% RSD	3.0	2.2	2.1	2.9	2.6	3.2	1.1	1.7	2.3	3.7	9.8	4.3	

Table 7. Summary for results from the high-level VOC study (concentrations in mg/L).						
	BENZ		M-XYL		PCE	
	Control	Sampler	Control	Sampler	Control	Sampler
Discrete Interval Sampler						
Mean	133	131	145	140	145	140
Standard deviation	1.1	2.3	3.3	3.4	4.1	3.1
% RSD	0.8	1.7	2.3	2.5	2.8	2.3
HydraSleeve						
Mean	137	136	148	144	144	142
Standard deviation	2.7	1.4	5.4	3.2	11.3	4.3
% RSD	2.0	1.0	3.6	2.2	7.8	3.0
Kabis Sampler						
Mean	137	138	151	149	153	147
Standard deviation	3.2	2.5	5.1	4.9	7.1	5.5
% RSD	2.3	1.8	3.4	3.3	4.6	3.8
Pneumo-Bailer						
Mean	130	132	142	140	142	138
Standard deviation	2.7	1.9	3.5	3.8	4.5	2.7
% RSD	2.1	1.4	2.5	2.7	3.2	1.9
Diffusion bag sampler						
Mean	108	114	99.7	108	94.7	105
Standard deviation	3.1	1.0	3.0	1.7	3.5	1.7
% RSD	2.8	0.9	3.0	1.6	3.7	1.6

With the PDB samplers, the differences tended to be larger. The contact times for the samplers were seven days in the high-level study and 23 days for the low-level study. In the low-level study, TDCE concentrations were significantly lower in the PDB samplers (10%) while concentrations of MXYL were significantly higher (18%). For the high-level study, concentrations of all three analytes were significantly higher in the bag samplers, but these differences were small (mean differences of 11% or less). Although it is possible that a longer equilibration time was needed at the higher concentrations, the time we allowed (seven days) was greater than the 24–48 hours equilibration times observed by

Vroblesky and Campbell (2001) for $\mu\text{g/L}$ and low mg/L concentrations. Therefore, we believe that the reason the more volatile compounds were slightly higher in the PDB samplers than in the standpipe was because they had volatilized from the test solution. (The standpipe in these experiments was covered but not sealed, and there were several inches of headspace.) Thus, the standpipe had lower concentrations of these analytes at the time of sampling (i.e., the controls) while the concentrations in the samplers reflected the previously higher concentrations in the standpipe. The more volatile compounds had the largest differences.

Metals study

The variability between replicate samples was very low ($<5\%$ RSDs), except for chromium concentrations in the PDB samplers where concentrations were very low (Table 8).

Concentrations of metals in samples taken with the Discrete Interval Sampler, HydraSleeve, Kabis Sampler, and Pneumo-Bailer were generally not significantly different from control values (Table 4). In the instances where there were significant differences, the differences were less than 6%.

However, as with the pesticides, there were dramatic differences between the metal concentrations in the PDB samplers and the controls. After 21 days' contact, three of the metals (As, Cd, Pb) were not detected in these samplers, and concentrations of Cr were approximately 95% lower. Again, these results support USGS guidance (Vroblesky 2001) that does not recommend using these devices for inorganic ions. However, we should mention that other membranes, such as the cellulose acetate (dialysis) membrane of the Multi-Level Sampler (available from Margan Ltd.), can be used to sample metals and anions (Ronen et al. 1986, 1987a, 1987b; Magaritz et al. 1989, 1990; Ronen and Magaritz 1989; Kaplan et al. 1991) or the Versapor membrane (acrylic copolymer coating over nylon fabric) can be used for sampling colloids (Weisbrod et al. 1996).

Analytical results from the field study

Again, even though these samples had to be brought over 130 feet to the surface and transferred to a sample vial, the variability was very low with the Discrete Interval Sampler, PDB samplers, and HydraSleeve, with RSDs less than 4% (Table 9). Slightly greater variability was observed with the Pneumo-Bailer and the Kabis Sampler, with 15% and 8% RSD, respectively. The RSD for the pumped control samples (using low-flow sampling) was less than 3%. With all these devices, mean concentrations were 5–14% lower than the mean values for the control samples.

Table 8. Metals study summary (concentration in µg/L).								
	Arsenic		Cadmium		Chromium		Lead	
	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler
Discrete Interval Sampler								
Mean	53	54	26.4	27.0	49	49	68	72
Std. Dev.	1.7	1.5	0.61	0.71	1.2	1.5	1.5	1.8
% RSD	3.1	2.8	2.3	2.6	2.5	3.1	2.2	2.5
HydraSleeve								
Mean	53	52	26.2	25.1	49	49	68	68
Std. Dev.	1.5	0.55	0.62	0.15	1.5	1.2	1.5	1.3
% RSD	2.8	1.1	2.4	0.6	3.1	2.5	2.2	1.9
Kabis Sampler								
Mean	53	53	26.7	26.4	49	48	71	70
Std. Dev.	0.55	0.45	0.62	0.49	2.3	0.71	0.84	1.3
% RSD	1.0	0.8	2.3	1.9	4.8	1.5	1.2	1.9
Pneumo-Bailer								
Mean	55	53	27.1	26.4	50	49	70	70
Std. Dev.	1.1	0.89	0.40	0.64	1.2	1.3	0.55	0.89
% RSD	2.0	1.7	1.5	2.4	2.4	2.7	0.8	1.3
Diffusion bag sampler								
Mean	53	<2.0	26.0	<2.0	49	2	70	<1.0
Std. Dev.	0		0.50		1.4	0.55	0	
% RSD	0		1.9		2.9	23	0	

With the HydraSleeve sampler, loss of TCE (11%) was statistically significant. Given that the sample had to be retrieved from such depth, it seems reasonable that losses of TCE might be slightly greater in this study than in the standpipe studies. These losses might possibly have been less if the HydraSleeve sampler had been left to equilibrate overnight prior to sampling, as recommended by the manufacturer.

Table 9. Summary of results from field study (concentration TCE in mg/L).

	Control	Discrete Interval Sampler
Mean	104	99.0
Std Dev.	2.15	4.16
% RSD	2.1	4.2
	Control	Kabis Sampler
Mean	101	99.0
Std Dev.	0.98	7.7
% RSD	1.0	7.8
	Control	PDB sampler
Mean	93.7	80.1
Std Dev.	0.84	0.62
% RSD	0.89	0.78
	Control	HydraSleeve
Mean	103	92.0
Std Dev.	2.7	2.6
% RSD	2.6	2.8
	Control	Pneumo-Bailer
Mean	97.7	90.4
Std Dev.	2.07	13.9
% RSD	2.1	15

We also observed a small (5%) but statistically significant loss of TCE using the Discrete Interval Sampler. In the previous VOC studies, we did not observe any significant losses with this device although in the low-level study, the loss of PCE was nearly 16%.

In contrast, the mean loss of TCE was 7.5% with the Kabis Sampler and Pneumo-Bailer, but these losses were not statistically significant. Our inability to determine a significant difference in this case can be attributed to the larger variability in sample concentrations that was observed with these devices. Previously in the standpipe study, we observed a fairly large and statistically significant loss of TCE with the Kabis Sampler. It is not surprising that there was larger variability with this sampler given that we heard the device bang against the wall of the well.

The mean concentration of TCE in the PDB samplers was significantly lower than in the controls after 23 days' contact. Although this difference is not large (14%), it may reflect a temporal shift in the water quality as a result of sporadic treatment at the site. However, it may also be that in spite of our best efforts, slow-flow sampling obtained a slightly different water sample. As mentioned previously, the mean concentrations for all five devices were lower than the equivalent mean for the control samples taken using slow-flow sampling.

One final note: both the Pneumo-Bailer and the Discrete Interval Sampler did occasionally yield what appeared to be anomalous results. We are not certain whether this indicates some type of malfunction and is reason for concern or not.

Leaving these devices in the well and allowing the well to recover prior to sampling could reduce the impact they have on the wells. The one exception to this would be the Kabis Sampler, which fills almost immediately after it stops in the well.

4 CONCLUSIONS AND RECOMMENDATIONS

The PDB samplers were the easiest to use of the samplers we tested. However, they should not be used to sample the larger, more hydrophobic explosive and pesticide compounds or metals. These findings support USGS guidance (Vroblesky 2001). Although we were not able to recover comparable concentrations of all of the VOCs in these studies, these differences were generally less than 15%. We believe that most of these differences occurred because this sampler yielded a time-averaged concentration rather than the concentration at the time of sampling.

The HydraSleeve samplers were also easy to operate but the up-and-down motion used to fill them apparently elevated the turbidity in our well. Although our standpipe studies indicated that this device generally yielded representative samples of pesticides, explosives, and metals, we would recommend using this device only in wells where the turbidity is not affected by its use. In some wells, this may mean redeveloping the well prior to using this device. The results from these studies indicate that there may be some small loss of volatiles when this device is used; loss of TCE in the field study was 11%. Leaving the sampler in the well overnight prior to sampling may reduce these losses.

The Kabis Sampler was relatively easy to deploy but the larger-sized device was heavy to recover. We observed bubbling in the standpipe and heard it bang against the wall of the standpipe and well, which apparently raised the turbidity in the well. This device recovered representative concentrations of explosives, pesticides, and metals in the lab studies. However, again, we would caution against using this device to sample for metals or hydrophobic organics such as pesticides in wells where the turbidity is affected by its use. Because there are concerns about the surging action within the well with large-diameter devices, we would recommend using a device that is considerably smaller in diameter than the well. In the standpipe studies, there were small, statistically significant differences between the concentrations of VOCs in the controls and samples taken with this device but the differences were both positive and negative, which indicates that there is not a strong bias in either direction. The exception to this was loss of TCE (one of the more volatile analytes) in the low-level study where loss was substantial, 18%. We also observed a relatively small (7.5%) loss of this analyte in the field study but this loss was not statistically significant. Einfield and Koglin (2000) also observed losses of the more volatile analytes, TCE and PCE, in a similar standpipe study.

The Discrete Interval Sampler was much easier to use than the Pneumo-Bailer. However, neither device appeared to disturb the well or elevate the turbidity when sampling, and the results from these studies indicate that these two devices are fairly comparable. In the standpipe experiments, both devices generally recovered representative concentrations of the explosives, pesticides, and metals. Any difference in the concentrations of the VOCs in samples taken with these devices vs. control samples was generally small, including the field study. However, during the course of the VOC and field studies, both devices did on occasion yield unusually low values that appeared to be anomalous, and this may be cause for concern.

One final concern we have is that because of an equipment problem, we did not monitor the effect these devices had on dissolved oxygen levels in the wells or standpipe. The operation of these devices, especially the Kabis Sampler and HydraSleeve, could affect this parameter and thereby affect the concentrations of oxygen-sensitive analytes.

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APPENDIX A: DATA SETS FOR REPLICATE SAMPLES

Table A1. Results from explosives study (concentrations in mg/L).													
Sampler	HMX		TNB		RDX		1,3 DNB		TNT		2,4 DNT		
	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control
Discrete Interval Sampler													
DI-1	0.525	0.540	2.20	2.15	4.81	4.91	0.113	0.115	1.92	1.94	0.0908	0.0925	
DI-2	0.530	0.515	2.18	2.16	4.79	4.73	0.114	0.111	1.92	1.90		0.0932	
DI-3	0.538	0.531	2.21	2.17	4.90	4.78	0.115	0.113	1.95	1.91	0.101		
Mean	0.531	0.529	2.20	2.16	4.83	4.81	0.114	0.113	1.93	1.92	0.0958	0.0928	
Pneumo-Bailer													
PB-1	0.519	0.525	2.22	2.21	4.76	4.81	0.112	0.112	1.91	1.92	0.088	0.088	
PB-2	0.527	0.526	2.18	2.17	4.78	4.74	0.113	0.113	1.91	1.91			
PB-3	0.516	0.522	2.18	2.20	4.72	4.80	0.111	0.112	1.89	1.92	0.097	0.088	
Mean	0.521	0.524	2.19	2.19	4.76	4.78	0.112	0.112	1.91	1.91	0.093	0.088	
HydraSleeve													
HY-1	0.519	0.541	2.24	2.14	4.77	4.82	0.112	0.114	1.91	1.91	0.0901		
HY-2	0.518	0.527	2.21	2.12	4.76	4.71	0.112	0.111	1.91	1.87	0.0943		
HY-3	0.523	0.532	2.20	2.17	4.72	4.79	0.112	0.112	1.90	1.90		0.0916	
Mean	0.520	0.533	2.217	2.14	4.75	4.774	0.112	0.113	1.91	1.89	0.0922	0.0916	
Kabis Sampler													
KA-1	0.529	0.513	2.25	2.21	4.77	4.69	0.113	0.111	1.92	1.90	0.0930	0.0995	
KA-2	0.522	0.533	2.27	2.27	4.81	4.87	0.113	0.115	1.93	1.96	0.102	0.102	
KA-3	0.514	0.517	2.23	2.23	4.73	4.73	0.111	0.111	1.90	1.89	0.0919	0.0958	
Mean	0.522	0.521	2.25	2.24	4.77	4.76	0.112	0.113	1.92	1.92	0.0956	0.0992	

Table A1 (cont'd). Results from explosives study (concentrations in mg/L).													
Sampler	HMX		TNB		RDX		1,3 DNB		TNT		2,4 DNT		
	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	
Diffusion bag sampler													
PDB-1	0.532	ND	1.88	0.356	4.62	ND	0.112	0.097	1.87	0.875	0.375	0.091	
PDB-2	0.534	ND	1.89	0.360	4.87	ND	0.112	0.097	1.88	0.881	0.375	0.087	
PDB-3	0.531	ND	1.88	0.351	4.86	ND	0.112	0.096	1.87	0.862	0.374	0.088	
Mean	0.532	ND	1.88	0.356	4.78	ND	0.112	0.097	1.87	0.873	0.375	0.089	

Table A2. Concentrations of samples in pesticides study.

	Lindane ($\mu\text{g/L}$)		Aldrin ($\mu\text{g/L}$)		Dieldrin ($\mu\text{g/L}$)	
	Control	Sampler	Control	Sampler	Control	Sampler
Discrete Interval Sampler						
1	489	553	21.9	23.5	46.9	48.6
2	561	486	31.3	30.5	43.3	40.1
3	556	462	27.1	25.5	48.1	45.9
4	591	508	35.1	32.8	48.2	45.2
5	772	694	36.3	35.9	49.5	48.2
Mean	594	541	30.3	29.6	47.2	45.6
HydraSleeve						
1	520	557	35.3	36.0	44.7	46.6
2	466	698	27.9	29.4	45.5	52.7
3	630	492	27.8	23.2	50.8	51.6
4	342	502	27.6	31.2	38.7	41.0
5	591	567	30.7	31.4	47.6	46.4
Mean	510	563	29.9	30.2	45.5	47.7
Kabis Sampler						
1	474	498	29.2	31.4	37.9	47.1
2	633	633	29.8	29.5	50.7	52.2
3	628	595	32.1	31.0	48.7	48.8
4	666	536	31.5	28.5	49.0	46.9
5	515	607	30.3	34.4	54.0	48.1
Mean	596	574	30.6	31.0	48.1	48.6
Pneumo-Bailer						
1	644	595	34.4	33.6	46.9	45.3
2	538	444	24.9	24.9	47.5	43.4
3	631	467	34.5	30.7	47.9	41.7
4	457	544	29.5	33.7	39.2	42.1
5	596	514	38.0	37.6	47.7	43.1
Mean	573	513	32.2	32.2	45.8	43.1

Table A2 (cont'd). Concentrations of samples in pesticides study.						
	Lindane ($\mu\text{g/L}$)		Aldrin ($\mu\text{g/L}$)		Dieldrin ($\mu\text{g/L}$)	
	Control	Sampler	Control	Sampler	Control	Sampler
Diffusion bag sampler						
A	443	501	29.8	25.7	27.4	3.2
B	554	330	31.9	16.2	33.1	1.2
C	683	681	36.4	29.8	32.8	27.4
Mean	560	504	32.7	23.9	31.1	10.6

Table A3. Concentrations (mg/L) of VOCs in the low-level study.												
TDCE		BENZ		TCE		ODCB		M-XYL		PCE		
Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	
HydraSleeve												
1	0.338	0.329	0.516	0.506	0.643	0.621	0.725	0.689	0.181	0.170	0.096	0.071
2	0.345	0.341	0.524	0.520	0.651	0.634	0.734	0.689	0.181	0.165	0.096	0.089
3	0.347	0.322	0.533	0.506	0.669	0.620	0.738	0.686	0.177	0.172	0.060	0.085
4	0.342	0.345	0.521	0.524	0.647	0.642	0.729	0.702	0.180	0.176	0.093	0.087
5	0.332	0.336	0.510	0.508	0.630	0.618	0.729	0.699	0.164	0.162	0.087	0.090
6	0.333	0.333	0.520	0.515	0.643	0.632	0.720	0.691	0.176	0.170	0.093	0.090
Mean	0.339	0.334	0.521	0.513	0.647	0.628	0.729	0.693	0.177	0.169	0.088	0.085
Kabis Sampler												
1	0.340	0.345	0.519	0.532	0.644	0.532	0.730	0.741	0.181	0.186	0.089	0.087
2	0.341	0.344	0.517	0.520	0.640	0.520	0.720	0.725	0.176	0.172	0.080	0.084
3	0.334	0.345	0.512	0.526	0.632	0.526	0.721	0.730	0.177	0.174	0.083	0.087
4	0.350	0.346	0.527	0.525	0.654	0.525	0.727	0.730	0.174	0.183	0.096	0.093
5	0.338	0.339	0.514	0.518	0.640	0.518	0.724	0.728	0.180	0.179	0.071	0.092
6	0.328	0.337	0.501	0.516	0.618	0.516	0.706	0.724	0.167	0.179	0.087	0.090
Mean	0.338	0.343	0.515	0.523	0.638	0.523	0.721	0.730	0.176	0.179	0.084	0.089
Pneumo-Bailer												
1	0.376	0.372	0.553	0.556	0.697	0.697	0.784	0.793	0.192	0.197	0.103	0.106
2	0.351	0.354	0.542	0.543	0.683	0.681	0.773	0.759	0.183	0.191	0.101	0.087
3	0.349	0.348	0.543	0.539	0.678	0.670	0.766	0.756	0.187	0.186	0.090	0.095
4	0.365	0.362	0.548	0.537	0.689	0.675	0.785	0.759	0.196	0.177	0.085	0.089
5	0.363	0.346	0.554	0.537	0.692	0.688	0.769	0.748	0.192	0.187	0.078	0.095
6	0.373	0.360	0.555	0.552	0.700	0.692	0.782	0.766	0.184	0.191	0.115	0.082
Mean	0.363	0.357	0.549	0.544	0.690	0.680	0.776	0.764	0.189	0.188	0.095	0.092

Table A3 (cont'd). Concentrations (mg/L) of VOCs in the low-level study.													
TDCE		BENZ		TCE		ODCB		M-XYL		PCE			
Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler
Discrete Interval Sampler													
1	0.348	0.358	0.550	0.562	0.678	0.698	0.792	0.803	0.187	0.196	0.101	0.100	
2	0.351	0.359	0.551	0.563	0.673	0.694	0.792	0.806	0.188	0.184	0.097	0.072	
3	0.360	0.362	0.564	0.567	0.703	0.707	0.811	0.809	0.202	0.200	0.103	0.090	
4	0.364	0.361	0.565	0.561	0.698	0.692	0.793	0.807	0.195	0.197	0.102	0.086	
5	0.363	0.353	0.571	0.556	0.710	0.690	0.809	0.805	0.202	0.200	0.104	0.057	
6	0.366	0.368	0.568	0.569	0.701	0.704	0.814	0.814	0.191	0.199	0.097	0.105	
Mean	0.359	0.360	0.562	0.563	0.694	0.698	0.802	0.807	0.194	0.196	0.101	0.085	
Diffusion Bag Sampler													
A	0.263	0.236	0.350	0.350	0.405	0.412	0.514	0.528	0.033	0.039	0.057	0.058	
B	0.248	0.226	0.336	0.335	0.386	0.391	0.506	0.514	0.033	0.037	0.048	0.054	
C	0.260	0.234	0.348	0.354	0.403	0.415	0.518	0.530	0.032	0.040	0.051	0.054	
Mean	0.257	0.232	0.345	0.346	0.398	0.406	0.513	0.524	0.033	0.039	0.052	0.055	

Table A4. Concentrations (mg/L) of VOCs in the high-level study.						
Discrete Interval Sampler						
	BENZ		M-XYL		PCE	
Sample No.	Control	Sampler	Control	Sampler	Control	Sampler
1	133	133	148	140	149	139
2	131	132	139	141	138	140
3	132	130	144	138	142	137
4	134	133	147	146	147	145
5	132	131	143	142	143	140
6	134	127	148	136	149	136
7	133		146		147	
Mean	133	131	145	140	145	139
HydraSleeve						
1	136	136	148	143	142	142
2	135	134	142	142	125	141
3	142	137	158	146	160	143
4	136	136	146	143	144	140
5	138	137	149	149	148	149
6	135	134	146	140	145	136
Mean	137	136	148	144	144	142
Kabis Sampler						
1	142	141	160	153	166	152
2	136	138	147	150	147	148
3	139	139	154	149	157	147
4	137	139	152	155	155	155
5	135	136	148	145	150	140
6	135	134	149	142	151	143
7	132		145		145	
Mean	137	138	151	149	153	147

Table A4 (cont'd).						
	BENZ		M-XYL		PCE	
Sample No.	Control	Sampler	Control	Sampler	Control	Sampler
Pneumo-Bailer						
1	130	134	143	141	142	141
2	132	133	144	138	145	137
3	133	134	147	146	148	142
4	128	130	140	136	140	137
5	128	131	140	140	138	139
6	126	130	137	136	136	135
Mean	130	132	142	139	142	138
Diffusion bag sampler						
A	109	114	100.1	109	95.1	106
B	105	113	96.6	106	91.0	103
C	111	115	102.5	109	97.9	106
Mean	108	114	99.7	108	94.7	105

Table A5. Concentrations (mg/L) of metals in samples.								
	Arsenic		Cadmium		Chromium		Lead	
	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler
Discrete Interval Sampler								
1	0.052	0.052	0.0264	0.0263	0.048	0.048	0.068	0.069
2	0.056	0.056	0.0269	0.0281	0.051	0.052	0.071	0.074
3	0.053	0.055	0.0254	0.0268	0.049	0.049	0.067	0.072
4	0.054	0.054	0.0269	0.0265	0.048	0.049	0.068	0.071
5	0.052	0.055	0.0263	0.0271	0.049	0.049	0.068	0.072
Mean	0.053	0.054	0.0264	0.0270	0.049	0.049	0.068	0.072
HydraSleeve								
1	0.051	0.052	0.0256	0.0251	0.048	0.049	0.067	0.070
2	0.053	0.051	0.0263	0.0250	0.051	0.049	0.068	0.067
3	0.052	0.051	0.0256	0.0253	0.048	0.048	0.067	0.068
4	0.053	0.052	0.0266	0.025	0.049	0.051	0.070	0.067
5	0.055	0.052	0.0270	0.0253	0.051	0.048	0.070	0.069
Mean	0.053	0.052	0.0262	0.0251	0.049	0.049	0.068	0.068
Kabis Sampler								
1	0.054	0.053	0.0268	0.0258	0.048	0.049	0.070	0.069
2	0.053	0.052	0.0267	0.0266	0.049	0.048	0.071	0.069
3	0.053	0.053	0.0259	0.0268	0.047	0.048	0.070	0.072
4	0.054	0.053	0.0276	0.0259	0.048	0.047	0.072	0.070
5	0.053	0.053	0.0264	0.0268	0.053	0.048	0.071	0.071
Mean	0.053	0.053	0.0267	0.0264	0.049	0.048	0.071	0.070
Pneumo-Bailer								
1	0.055	0.052	0.0271	0.0268	0.052	0.048	0.071	0.069
2	0.053	0.054	0.0272	0.0266	0.049	0.050	0.070	0.071
3	0.056	0.053	0.0269	0.0253	0.050	0.047	0.070	0.071
4	0.055	0.054	0.0276	0.0269	0.050	0.050	0.071	0.070
5	0.055	0.054	0.0265	0.0264	0.049	0.049	0.070	0.071
Mean	0.055	0.053	0.0271	0.0264	0.05	0.049	0.070	0.070

Table A5 (cont'd).								
	Arsenic		Cadmium		Chromium		Lead	
	Control	Sampler	Control	Sampler	Control	Sampler	Control	Sampler
Diffusion bag sampler								
A	0.053	<0.002	0.0265	<0.0002	0.050	0.003	0.069	<0.001
B	0.053	<0.002	0.0264	<0.0002	0.050	0.003	0.070	<0.001
C	0.053	<0.002	0.0257	<0.0002	0.048	0.002	0.070	<0.001
Mean	0.053	<0.002	0.0260	<0.002	0.049	0.002	0.070	<0.001

Table A6. Concentrations of TCE (mg/L) in samples taken during field study.

Sample #	Control-DI	DI Sampler	Control-H	HydraSleeve
1	104.5	92.0	100.9	95.0
2	105.8	98.0	104.0	94.5
3	105.7	97.9	98.5	90.8
4	106.7	99.6	103.5	87.4
5	100.7	102.2	104.4	92.8
6	103.7	104.0	106.3	92.2
7			105.5	91.2
Mean	104.5	99.0	103.3	92.0
Sample #	Control-K	Kabis	Control-PB	Pneumo-Bailer
1	101.2	107.6	94.0	93.9
2	99.8	96.1	99.0	93.5
3	101.9	97.8	98.5	99.9
4	100.9	87.1	96.5	67.1
5	101.8	107.3	98.9	105.8
6	99.6	97.9	99.2	82.0
Mean	100.9	99.0	97.7	90.4
	Control- PDB	PDB Sampler		
DS-A	94.7	80.3		
DS-B	93.4	79.5		
DS-C	93.2	80.7		
Mean	93.7	80.1		

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14. ABSTRACT Five relatively newly developed groundwater-sampling devices (the Kabis, HydraSleeve, Discrete Interval, Pneumo-Bailer, and USGS Passive Diffusion Bag [PDB] samplers) were tested to determine their ability to recover representative concentrations of a variety of analytes, including volatile organics, explosives, pesticides, and metals. The first phase of the study included several standpipe experiments with known concentrations of analytes. In the second phase, the devices were used in the field to sample TCE from a deep well and were compared with samples taken using low-flow sampling. We found that the PDB sampler was the easiest device to use but should be used only for selected VOCs. The HydraSleeve and the Kabis Sampler are thief-type samplers that were also relatively easy to use. Although these devices could produce representative concentrations of explosives, pesticides, and metals in the standpipe experiments, they elevated the turbidity in our monitoring well. Therefore, we would recommend that their use be limited to wells where the turbidity is not affected by their use, especially if sampling for metals or the more hydrophobic organic contaminants. In addition, there were small but statistically significant losses of some VOCs with the HydraSleeve in the standpipe studies (<5%) and of TCE in the field study (11%). Concentrations of VOCs taken with the Kabis Sampler did not show a substantial and consistent bias in either direction, except for the low-level study where loss of TCE was substantial, 18%. In the field study, loss of TCE was small (<8%) with this device and not statistically significant. The Discrete Interval Sampler and Pneumo-Bailer are pressurized thief-type devices that are designed to collect a sample when activated. The Pneumo-Bailer was heavy and awkward to handle, required taking a nitrogen tank into the field, and was difficult to operate. The Discrete Interval Sampler required only a bicycle pump to pressurize the chamber, was smaller and lighter in weight, and easier to handle and operate than its counterpart. Both devices generally delivered representative concentrations of all the analytes tested in the standpipe experiments. Although loss of TCE was statistically significant for the Discrete Interval Sampler in the field study, loss was very small (<5%).					
15. SUBJECT TERMS					
Discrete Interval Sampler Discrete interval samplers		Groundwater samplers Groundwater sampling		HydraSleeve Kabis Sampler	
				Passive diffusion bag samplers Pneumo-Bailer	
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